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(54) Title of the Invention

METHOD FOR MANUFACTURING CYCLIC ETHER

(57) Abstract

[PURPOSE] To obtain a cyclic ether such as THF and oxetane under a relative mild condition, by using a heteropoly acid as a catalyst, and cyclizing an alcohol containing two hydroxyl groups in the molecule or its acetic acid ester.

[CONSTITUTION] A novel catalyst, consisting of a heteropoly acid such as phosphomolybdic acid and phosphotungstic acid, and its salts, having low corrosive properties, low deterioration in activity, and stability for a long period, is used, a dihydric alcohol (for example, 1,3-propanediol, etc.) or a dihydric alcohol acid ester (monoacetic ester, or diacetic acid ester) is reacted and cyclized at 70W 250 degrees C, preferably at 100W 200 degrees C to give a cyclic ether. The reaction product is readily separated from both the catalyst and a raw material by distillation.

CLAIMS

1. A method for manufacturing cyclic ether by using heteropoly acid and its salts as a catalyst, and cyclizing alcohol, containing two hydroxyl groups in the molecule, or by cyclizing acetic acid ester of such alcohol.
2. A method according to claim 1 wherein said alcohol is such alcohol that the two hydroxyl groups are isolated by three to six carbon atoms.

[Detailed description of the Invention]

[Field of Invention]

The present invention relates to a method using a new catalyst for manufacturing cyclic ether by cyclizing alcohol having two hydroxyl groups in the molecule (hereinafter referred to as "dihydric alcohol") or by cyclizing acetic acid ester of the dihydric alcohol.

Cyclic ethers such as tetrahydrofuran (hereinafter referred to as the "THF") and oxetane are important chemical compounds for industrial purposes to be used as solvents or raw materials for high polymer compounds and organic chemicals.

[Prior Art]

For a method to synthesize cyclic ether, a method to cyclize dihydric alcohol or acetic acid ester of the dihydric alcohol by using sulfuric acid, alumina, etc. as the catalyst has been well known (L.F. Schmoyer, L.C. Case, *Nature*, **187**, 592 (1960), Y. Inoue, S. Deguchi, and T. Hakushi, *Bull. Chem. Soc. Jpn.*, **53**, 3031 (1980), JP Publication No. S53-43506).

[Problem to be Solved by the Invention]

However, the catalysts described in the above are desired to be improved since each of them has disadvantages. More specifically, with the acetic acid, the chemical reactions are not mild and the reaction fluid is significantly tinted. Furthermore, it is difficult to separate the catalyst from reaction products, and the reactor vessel is significantly corroded with the catalyst. With the alumina, it needs to be reacted in a high temperature and high voltage environment.

[Means for Solving the Problem]

Inventors of the present invention, as a result of dedicating to studying catalysts which enables reactions under comparatively mild conditions and offers less causticity, found heteropoly acid and its salts as catalysts that satisfy such conditions, thus achieving the present invention.

More specifically, the present invention refers to a method for manufacturing cyclic ether by using heteropoly acid and its salts as a catalyst, and cyclizing alcohol, containing two hydroxyl groups in the molecule, or by cyclizing acetic acid ester of such alcohol.

The heteropoly acid and its salts according to the present invention are heteropoly acid which is a generic name of oxyacids and its salts that are produced through a condensing between at least one oxide of Mo, W and V, and oxiaacid of other elements, for example, P, Si, As, Ge, B, Ti, Ce, Co, etc.

Specific example of such heteropoly acid and its salts include phosphomolybdic acid, phosphotungstic acid, phosphomolybdo-tungstic acid, phosphomolybdo-vanadic acid, phosphomolybdo-tungsto-vanadic acid, phosphotungsto-vanadic acid, phosphomolybdo-niobic acid, silicotungstic acid, silicomolybdic acid, silicomolybdo-tungstic acid, silicomolybdo-tungsto-vanadic acid, germanium-tungstic acid, borictungstic acid, boricomolybdic acid, boricomolybdo-tungstic acid, boricomolybdo-vanadic acid, boricomolybdo-tungsto-vanadic acid, cobalticomolybdic acid, cobaltictungstic acid, arsenicomolybdic acid, arsenictungstic acid, titanicomolybdic acid, cericomolybdic acid and their salts. Types of salt are not specifically limited, but they include salts of series I metals in the periodic table such as Li, Na, K, Rb, Cs, Cu, Ag, and Au, salts of series II metals such as Mg, Ca, Sr, Ba, Zn, Cd and Hg, salts of series III metals such as Sc, La, Ce, Al, Ga, and In, salts of series VIII metals such as Fe, Co, Ni, Ru, Pd, and Pt, and salts of metals such as Sn, Pb, Mn, and Bi, or ammonium salts, amine salts, etc. of such metals.

The exemplification of these salts includes 12-tungstophosphoric-acid-1-lithium ($\text{LiH}_2\text{PW}_{12}\text{O}_{40}$), 12-tungstophosphoric-acid-2-sodium ($\text{Na}_2\text{HPW}_{12}\text{O}_{40}$), 12-tungstophosphoric-acid-2-karium ($\text{K}_2\text{H}_2\text{PW}_{12}\text{O}_{40}$), 12-tungstophosphoric-acid-2-cesium ($\text{Ce}_2\text{HPW}_{12}\text{O}_{40}$), 12-tungstophosphoric-acid-1-silver ($\text{AgHPW}_{12}\text{O}_{40}$), 12-tungstophosphoric-acid-1-magnesium ($\text{MgHPW}_{12}\text{O}_{40}$), 12-tungstophosphoric-acid-1-calcium ($\text{CaHPW}_{12}\text{O}_{40}$), 12-tungstophosphoric-acid-1-zinc ($\text{ZnHPW}_{12}\text{O}_{40}$), 12-tungstophosphoric-acid-1-aluminum ($\text{AlPW}_{12}\text{O}_{40}$), 12-tungstophosphoric-acid-1-gallium ($\text{GaPW}_{12}\text{O}_{40}$), 12-tungstophosphoric-acid-1-indium ($\text{InPW}_{12}\text{O}_{40}$), 12-tungstophosphoric-acid-1-chrome ($\text{CrPW}_{12}\text{O}_{40}$), 12-tungstophosphoric-acid-1-

bismuth ($\text{BiPW}_{12}\text{O}_{40}$), 12-tungstophosphoric-acid-1-iron ($\text{FePW}_{12}\text{O}_{40}$), 12-tungstosilicic-acid-1-nickel ($\text{NiHSiW}_{12}\text{O}_{40}$), 12-tungstosilicic-acid-2-lithium ($\text{Li}_2\text{H}_2\text{SiW}_{12}\text{O}_{40}$), 12-tungstosilicic-acid-2-silver ($\text{Ag}_2\text{H}_2\text{SiW}_{12}\text{O}_{40}$), 12-tungstosilicic-acid-1-magnesium ($\text{Mg}_2\text{H}_2\text{SiW}_{12}\text{O}_{40}$), 12-tungstosilicic-acid-1-aluminum ($\text{AlHSiW}_{12}\text{O}_{40}$), 12-tungstosilicic-acid-1-indium ($\text{InHSiW}_{12}\text{O}_{40}$), 12-tungstosilicic-acid-1-gallium ($\text{GaHSiW}_{12}\text{O}_{40}$), 12-tungstophosphoric-acid-1-lithium ($\text{LiH}_2\text{PMo}_{12}\text{O}_{40}$), 12-tungstophosphoric-acid-1-magnesium ($\text{MgHPMo}_{12}\text{O}_{40}$), 12-tungstophosphoric-acid-2-ammonium $[(\text{NH}_4)_2\text{HPW}_{12}\text{O}_{40}]$, 12-tungstophosphoric-acid-2-ammonium $[(\text{NH}_4)_2\text{HPW}_{12}\text{O}_{40}]$, 12-tungstosilicic-acid-1-tetramethylamine $[\text{N}(\text{CH}_3)_4\text{HSiW}_{12}\text{O}_{40}]$, etc. In addition, a mixture of heteropoly acid and its salts may be used. The heteropoly acid salts are prepared by titrating the water solution of heteropoly acid with a carbonate of various metals or nitrate salt, ammonia or amine, and then by evaporating the solution.

Normally, the heteropoly acid and the salts are synthesized as a 20-40 hydrate. Under this status, the activity of the hydrant is extremely low, but it will become higher as water is being removed out of the system by distillation, etc. For the reaction to obtain cyclic ether by dehydrating and cyclizing dihydric alcohol, water is generated within the system. Therefore, it is preferable to achieve the reaction while removing water by means of distillation, etc. to sustain the activity of catalyst. In addition, water is necessary for the reaction to cyclize acetic ester of dihydric alcohol, but it is desirable that the reaction should be achieved by adding required amount of water continuously or intermittently while removing surplus water by means of distillation, etc. Dehydrating the heteropoly acid or its salts used as a catalyst to reduce the number of coordinated water down to 15 or less, preferably 8 or less, or more preferably 4 or less before initiating the reaction is desirable because the activity can be much more intensified than the initial status. The control of the number of coordinated water is possible by heating heteropoly acid or its salts to a high temperature or by keeping them under the reduced pressure conditions at comparatively low temperature.

Although the quantity of heteropoly acid or its salts to be used is not specifically limited, when the quantity of heteropoly acid or its salts in the reactor vessel, the reaction speed will become slow, and therefore, they should be used in quantity of 0.005 to 5.0 times in weight, or preferably 0.01 to 1.0 times, as that of dihydric alcohol or acetic ester of dihydric alcohol available in the reactor vessel.

There is no specific limitation for the dihydric alcohol used as a raw material according to the present invention, but preferably, it may preferably be such dihydric alcohol wherein two hydroxyl groups are isolated by three to six carbon atoms.

Examples of such dihydric alcohol include 1,3- propanediol, 1,4-butanediol, 1,4-dihydroxy-2-butene, 1,3-butanediol, 1,5-pentanediol, 1,6-hexanediol, 2,5-hexanediol, 2,5-dihydroxy-3-hexene, neopentylglycol, 1,2,6-hexanetriol, diethylene glycol, etc. Examples of acetic ester of dihydric alcohol include mono-acetic ester and di-acetic ester of the above-stated dihydric alcohol.

For the reaction temperature, 70 degrees C to 250 degrees C, or more preferably, 100 degrees C to 200 degrees C will be applied. At temperatures below 70 degrees C, the yield of cyclic ether will be lowered, and at temperatures above 250 degrees C, dihydric alcohol will be dissolved or side reactions are likely, both of which are not desirable. It is preferable to achieve a reaction at a temperature below the boiling point of dihydric alcohol or acetic ester of dihydric alcohol, and at a temperature that enables to remove cyclic ether, acetic acid and water to be generated by means of distillation, since such reaction only allows the heteropoly acid to be used in a highly activated status and the raw materials and products to be separated at the same time.

The quantity of water to be used in the reaction to cyclize acetic ester of dihydric alcohol should be in the range of 0.5 to 50 moles, or more preferably 0.5 to 10 moles per acetic ester group of dihydric alcohol.

It is desirable to perform the reaction while removing cyclic ether and acetic acid to be produced during the reaction in terms of the equilibrium. The reaction can either be performed under atmospheric pressure, reduced pressure or pressurized conditions.

The form of catalyst used in the above-stated reaction depends on the status of conditioned water or reaction conditions, and the catalyst exists in either the evenly-dissolved form in the reaction fluid, solid-state

form or fluid and further in the state that forms two phases along with the reaction fluid. In either form, however, the catalyst does not have a steam pressure, and the reaction should be carried out while stirring the raw materials and the catalyst. The products can be removed from the reactor vessel by means of distillation. Although catalyst is not specifically required, inactive substances may be added in the reaction.

Time required for the reaction depends on the quantity of catalyst and the reaction temperature, but it is in the range from 0.5 to 20 hours.

As for the reaction system, either of the batch system which uses popular reactor vessel featuring mixing and stirring functions or the continuous system may be employed.

In addition, in a case where the catalyst is supported by activated carbon, silica-alumina, etc. under a well-known method, or if the catalyst is of solid-state in the reaction system, it may be used as is as a fixed bed, or the supported catalyst may be used as a fluidized bed.

[Effects of the Invention]

In the method according to the present invention, it is possible to synthesize cyclic ether by using dihydric alcohol or acetic ester of dihydric alcohol under a comparatively mild conditions, and products can easily be separated from catalyst and raw materials by means of distillation. Since a catalyst to be used in the present invention features less causticity and the activity is less deteriorated, it may be stably used for a long period of time.

[Best Mode of Carrying Out the Invention]

Hereinafter, the present invention will be described with reference to preferred embodiments.

First Embodiment

Two hundred grams of 1,4-butanediol is put in a three-neck flask which is equipped with a stirrer, a temperature gauge and a dispensing cooling unit. Then, add 10g of phosphotungstic acid ($H_3PW_{12}O_{40}$) which has been made anhydrous by heating it at 300 degrees C for three hours, and further heat it up to 120 degrees C while stirring the mixture. The reaction will progress immediately, and the THF and water generated will flow out of the system. After allowing the reaction to continue for two hours, 95% of the 1,4-butanediol in the flask was dissolved into the THF and water to be flowed out of the system.

Second Embodiment

Two hundred grams of 1,4-butanediol was put in a three-neck flask which is described in the first embodiment. Then, 10g of heteropoly acid or its salts, shown in Table 1, which had been made anhydrous by heating it at a high temperature was added. The mixture was heated up to 120 degrees C while stirring it at the same time, and the flow-out quantity of the THF was measured after two hours. Table 1 shows the results.

Table 1

Heteropoly Acid and its Salts	Inversion Rate to THF (%)
$H_3PMo_{12}O_{40}$	88
$H_6P_2Mo_{12}O_{62}$	84
$H_3PMo_9O_{31}$	78
$H_3PVMo_{11}O_{40}$	83
$H_4SiW_{12}O_{40}$	94
$H_6P_2W_{15}O_{62}$	90
$H_3AsW_{12}O_{40}$	73
$H_4SiMo_{12}O_{40}$	82
$H_4GeW_{12}O_{40}$	79
$H_6BW_{12}O_{40}$	81
$AlPW_{12}O_{40}$	79
$CrPW_{12}O_{40}$	83
$LiH_2PW_{12}O_{40}$	75
$Na_2H_2SiW_{12}O_{40}$	76
$Cs_2HPW_{12}O_{40}$	72

Third Embodiment

Ten grams of phosphotungstic acid ($H_3PW_{12}O_{40}$) which has been made anhydrous by heating it at 300 degrees C for three hours, and 100g of dihydric alcohol and its salts, as shown in Table 2, were put in a three-neck flask which is described in the first embodiment. The mixture was stirred for a specified period of time at temperatures shown in Table 2, and cyclic ether and water generated were distilled. Table 2 shows the results.

Table 2

Dihydric Alcohol	Reaction Conditions		Cyclic Ether	Inversion Rate (%)	Selection Rate (%)
	Temp (degrees C)	Hours (hr)			
1,3-propanediol	170	3.5		45	1.2
Neopentylglycol	170	3.5		65	35
1,5-pentanediol	140	2.0		92	100
1,6-hexanediol	170	2.5		51	78
Diethylene glycol	170	3.5		75	81

Fourth Embodiment

Ten grams of phosphotungstic acid ($H_3PW_{12}O_{40}$) which had been made anhydrous by heating it at 300 degrees C for three hours, and 100g of acetic acid of dihydric alcohol shown in Table 3, were put in a three-neck flask which is described in the first embodiment. The mixture was stirred at a temperature of 130 degrees C. Then, 30g of water was continuously added in two hours. The reaction was allowed for another one hour after the completion of the adding, then the cyclic ether and acetic acid that were generated and flowed out of the system were analyzed and determined the quantity. Table 3 shows the results.

Table 3

Acetic Acid Ester	Cyclic Ether	Yield of Cyclic Ether (%) ^{*1}
1,4-diacetoxybutane		88
1,4-diacetoxy-2-butene		82

*1) Yield = Number of moles of cyclic ether generated / number of moles of acetic acid ester put in the flask x 100

Fifth Embodiment

One hundred grams of 1,4-butanediol and 15g of tungstosilicic-acid ($H_4SiW_{12}O_{40}$) which had been made anhydrous by heating it at 300 degrees C for three hours, were put in a four-neck flask which is equipped with a stirrer, a temperature gauge, a dispensing cooling unit, and an opening for feeding raw materials. The reaction temperature was set at 130 degrees C while continuously stirring the mixture. The reaction will progress immediately, and the THF and water generated will flow out of the system. Then, 1,4-butanediol was continuously fed at the speed of 100g/hour, and the reaction was carried out continuously while extracting the THF and water generated out of the system. Operation was continued for 50 hours, and 5.0kg of the THF which contains approximately 20% of part weight was obtained.

Sixth Embodiment

One hundred grams of 1,4-butanediol and 30g of phosphotungstic acid ($H_3PW_{12}O_{40}$) which had been made anhydrous by heating it at 300 degrees C for three hours, were put in a stainless steel pressurized reactor vessel. The reaction was allowed for two hours while continuing the stirring with the reaction temperature set at 150 degrees C. After the completion of the reaction, the fluid remaining in the reactor vessel was analyzed with the gas chromatograph to give 40g of non-reactive 1,4-butanediol and 48g of the THF.

Shimizu Takeshi, Representative (Seal)

Written Amendment

February 22, 1985

To: Shiga Manabu, Director-General of the Patent Office

1. Indication of Affair
JP Application No. S59-244334
2. Title of the Invention
Method for Manufacturing Cyclic Ether
3. Person to make the amendment
Relationship with the affair/Applicant
(003) Asahi Chemical Industry Co., Ltd.
4. Representative
Toranomon Sangyo Building 5F
2-29 Toranomon 1-chome, Minato-ku, Tokyo
(6823) Shimizu Takeshi, Patent Attorney
5. Part to be Amended
The section of Detailed Description of the Invention of Specification
6. Details of the Amendment
"H₃PVMo₁₁O₄₀" on the fourth row from the top of the column of Heteropoly Acid and its Salts in Table 1 on page 12 of the Specification shall be amended to "H₄PVMo₁₁O₄₀".

Shimizu Takeshi, Representative (Seal)

Written Amendment

April 25, 1985

To: Shiga Manabu, Director-General of the Patent Office

1. Indication of Affair
JP Application No. S59-244334
2. Title of the Invention
Method for Manufacturing Cyclic Ether
3. Person to make the amendment
Relationship with the affair/Applicant
(003) Asahi Chemical Industry Co., Ltd.
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(6823) Shimizu Takeshi, Patent Attorney
5. Date of Order for Amendment
March 26, 1985
6. Part to be Amended
The section of Detailed Description of the Invention of Specification
7. Details of the Amendment
 - (1) "(L.F. Schmoyer, JP Application No. S53-43506) on the 8th to 10th lines on page 2 of the Specification shall be amended as follows:
"(L.F. Schmoyer, L.C. Case, Nature), 187, 592 (1960), (Y. Inoue, S. Deguchi, and T. Hakushi, Bull. Chem. Soc. Jpn.), 53, 3031 (1980), JP Application No. S53-43506)."

Shimizu Takeshi, Representative (Seal)